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(54) **Organic film-coated plated steel sheet and process for its production**

Mit organischem, filmbeschichtetes plattiertes Stahlblech und Verfahren zu dessen Herstellung

Tôle d'acier galvanisée revêtue d'un film organique et procédé pour sa fabrication

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**EP-A- 0 531 575** **FR-A- 2 698 380**

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**Description****BACKGROUND OF THE INVENTION**5 **Field of the Invention**

**[0001]** This invention relates to a process for the production of an organic film-coated plated steel sheet which sheet excels in corrosion resistance, weldability, electrodeposition ability or paint adhesion.

10 **Description of the Related Art**

**[0002]** An increasing number of steel sheet treated on their surfaces have recently been applied to the automotive industry to comply with demands for automobile bodies having enhanced resistance to corrosion. Such a surface-treated steel sheet is typified by a zinc-plated steel sheet, a zinc alloy-plated steel sheet and the like. Moreover, a greater magnitude of corrosion resistance has been required for bag structures and bent or hemmed portions disposed inwardly of the automobile body and exposed to wet conditions since the bags and hems are often difficult to paint completely subsequent to assembly of the body.

**[0003]** Certain steel sheet has been proposed to meet the above noted requirements as disclosed for instance in Japanese Unexamined Patent Publication Nos. 3-130141 and 2-258335. They are of a multi-layered type having a zinc-or zinc alloy-plated steel sheet, a chromate layer and an organic polymer layer superimposed in that order. The organic polymer layer contains silica and has a coating thickness of not more than several microns ( $\mu\text{m}$ ). This type of steel sheet offers markedly excellent corrosion resistance even without the need for painting after assembly of the automobile body and, hence, has predominated in forming inner surfaces of the body.

**[0004]** For economic reasons the automotive industry has been compelled to effect further reductions in production costs.

**[0005]** The multi-layered steel sheet stated above is produced by treating a base steel sheet with zinc-based plating, followed by formation of a chromate film and an organic film on the steel sheet. Such mode of production uses a coater and a baking oven, respectively, for Zn-base plating, chromate film formation and organic film formation. Plating equipment is completely structurally different from coating and baking equipment. They have varying speeds of production lines and variable factors of production controls. In a commonly practiced production system, therefore, coiling is first performed after completion of Zn-base plating. Subsequent processing is conducted in coating and baking equipment installed separately from the plating equipment. This involves additional equipment and facilities as well as considerable increase in production cost, thereby forcing both automobile and steel manufacturers to shoulder heavy burdens.

**[0006]** According to the present invention, an organic film-coated steel sheet can be obtained with reserve tanks for Zn-base plating and post-treatment facilities utilized to good advantage and without incurring further construction costs. For example, a plating line alone leads to the production or coiling of the desired coated steel, resulting in a noticeable decline in production cost. In other words, the method of the invention allows the existing equipment, if provided with plating facilities, easily to switch over from the formation of a plated steel sheet to the production of an organic film-coated steel sheet that has conspicuously excellent resistance to rust.

**[0007]** Electrodeposition painting is in common use for the formation of organic films on the surfaces of steel sheet by means of electrolysis. Electrodeposition painting is a method in which an aqueous solution containing a water-based or emulsified polymer and a pigment is subjected to electrical charging, whereby the polymer and pigment migrate and are separated out. Electrodeposition painting is less effective than coaters in achieving thickness uniformity. In the case of formation of an organic film with a thickness of several tens of microns ( $\mu\text{m}$ ), a slight thickness irregularity may be tolerable.

**[0008]** It is necessary, however, for use in automobiles, for the organic film to be coated on the steel sheet at no more than several microns ( $\mu\text{m}$ ) in thickness so as to ensure good subsequent weldability. In such a thin-walled film, thickness uniformity has a strong effect on corrosion resistance. For this and other reasons, electro-deposition coating is unacceptable; it results in increased cost and needs further operations including baking after coating, and high-voltage electrolysis treatment.

**[0009]** Electrolytic polymerization is another means for forming an organic film by electrolysis. This mode of polymerization uses a monomer as a starting material. The monomer is caused to polymerize, through electrolysis, simultaneously with film formation with eventual coating of an organic polymer film directly over the substrate. Electrolytic polymerization has in recent years found rapid application, mainly in the fields of condensers and electronic components as disclosed for example in Japanese Examined Patent Publication Nos. 3-65008, 3-61314 and 4-7521. These publications each pertain to an organic film with particular emphasis upon the characteristic of electrical conductivity, but fail to consider corrosion resistance or to teach that such films could render the corresponding substrate anticorrosive.

**[0010]** Japanese Examined Patent Publication No. 50-15485 and Japanese Unexamined Patent Publication No.

55-16075 each disclose a method of surface-treating a metal structure by directly forming an electrolytically polymerized film over the surface of the metal. Each such method is contrived as a replacement for electrodeposition painting to attain cost savings by omitting the usual baking operation and reducing electrical requirements, namely by reducing voltage. In those references organic films are coated over the surface of an electrically conductive substrate by electrodeposition or by coater means, in most cases, to achieve corrosion resistance or otherwise improve rustproofness. The rustproofness property results from insulation, impermeability to water and oxygen and the like, and the organic film should have a thickness of not more than several tens of microns ( $\mu\text{m}$ ), thereby gaining the insulation and impermeability properties closely associated with rustproofness.

[0011] In the case where electrolytic polymerization is employed in forming an organic film, insulation and rust resistance may be obtained, as disclosed in Japanese Examined Patent Publication No. 50-15485 above, but only by prolonged electrolysis. Furthermore, as the film thickness increases, higher voltage is required to compensate for resistance of the film thickness. This makes film formation difficult. It also results in increased electrical usage. This means that cost savings flowing from omitted baking operations become substantially offset. To add to those problems, suitably useful or electrolytically polymerizable monomers are restrictive, and the resultant polymers are incapable of modification and crosslinking. Consequently, electrolytic polymerization is still unfeasible for practical purposes as providing a substitute for a general organic film made to have rust resistance through insulation.

[0012] FR-A-2 698 380 discloses a method for preparing a polypyrrole coating on a metallic substrate by anodic electropolymerization, said metallic substrate being a pretreated zinc based substrate, which is obtained by bringing into contact a zinc based substrate with a liquid medium containing at least one sulfide in solution, immersing said substrate pretreated in an aqueous electrolytic bath containing oxalate ions and at least one polymerizable pyrrole compound, and applying a continuous current by means of an electric generator and a counter electrode, using said pretreated substrate as anode, at a tension sufficient for provoking the anodic electropolymerization of said pyrrole compound.

## OBJECTS OF THE INVENTION

[0013] In order to solve the foregoing problems of the prior art, the present invention has for one of its primary objects to provide a process for producing a new organic film-coated plated steel sheet which is resistant to corrosion, weldable, paintable by electro-deposition or adhesive to paints, and is excellent as a rustproof steel sheet particularly for use in automobile bodies, with fewer equipment requirements and reduced production cost.

[0014] Other objects and advantages of the invention will become apparent to those skilled in the art from the drawings, the detailed description of the invention and the appended claims.

## SUMMARY OF THE INVENTION

[0015] According to one important aspect of the invention, there is provided a process for the production of an organic film-coated plated steel sheet, which comprises the steps of:

plating a zinc-based metal on either one or both surfaces of a steel sheet to form a zinc-based plated steel sheet; and subsequently carrying out a cathodic polymerization of at least one organic monomer in an electrolytic liquid to form an organic film on said zinc-based plated steel sheet.

[0016] Said organic film-coated plated steel sheet comprising a steel sheet, a zinc-based plated layer disposed thereon, with or without an optional overlayer containing chromium, and an organic film layer is formed by cathodic polymerization of at least one monomer and polymerized on the outermost layer. The organic film-coated plated steel sheet preferably includes a chromium containing layer interposed between the zinc-base plated layer and the organic film layer. Preferably, the zinc-based plated layer is deposited in an amount of 10 to 90 g/m<sup>2</sup> on the steel sheet, and the organic film layer is polymerization coated in an amount of 0.01 to 3 g/m<sup>2</sup>. It is further preferred that the zinc-based plated layer is deposited in an amount of 10 to 90 g/m<sup>2</sup>, the chromium containing layer is coated in an amount of 10 to 500 mg/m<sup>2</sup> expressed as Cr, and the organic film layer is coated in an amount of 0.01 to 3 g/m<sup>2</sup>.

[0017] In this invention an intervening layer containing Zn or Cr is provided as a site for polymerization of the monomer. The monomer is preferably selected from the group consisting of vinyl pyridine, acrylic acid, methacrylic acid, acrylic acid ester, methacrylic acid ester, acrylonitrile, styrene, crotonic acid, acetonitrile, and derivatives thereof.

[0018] Preferably, the process of this invention further includes the intermediate step of treating the zinc-based plated steel sheet with a chromium containing compound, and subsequently carrying out electrolytic polymerization in an electrolytic liquid containing at least one monomer, thereby polymerizing an organic film layer on the chromium containing compound-treated steel sheet. Zinc-based plating may be deposited in an amount of 10 to 90 g/m<sup>2</sup>, and the

organic film may be applied in an amount of 0.01 to 3 g/m<sup>2</sup>. Further, the zinc-based plating step is desirably conducted with a deposit of 10 to 90 g/m<sup>2</sup>, the chromium containing compound treatment with an amount of 10 to 500 mg/m<sup>2</sup> expressed as Cr, and the organic film formation 0.01 to 3 g/m<sup>2</sup>.

[0019] In cathodic polymerization the monomer may be selected from the group consisting of vinyl pyridine, acrylic acid, methacrylic acid, acrylic acid ester, methacrylic acid ester, acrylonitrile, styrene, crotonic acid and acetonitrile, and derivatives thereof.

[0020] The cathodic polymerization is preferably effected at a current density of not lower than 1 A/dm<sup>2</sup> and for an electrolytic time of not longer than 10 seconds.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0021] FIG. 1 is a schematic view showing the shape of an organic film formed on a steel sheet by coater means.

[0022] FIG. 2 is a view similar to FIG. 1, but showing an organic film formed by cathodic polymerization.

#### DETAILED DESCRIPTION OF THE INVENTION

[0023] It will be appreciated that the following description is intended to refer to the specific embodiments of the invention selected for illustration in the drawings and as described in the Examples and is not intended to limit the invention, other than in the appended claims.

[0024] The organic film-coated plated steel sheet according to the present invention is most preferably used for automobiles, although many other uses are possible. To this end, the organic film should still be weldable, or paintable by electrodeposition as discussed hereinabove. In order to meet these requirements the organic film needs to have exceptionally small thickness, say of not more than the order of several microns ( $\mu\text{m}$ ). This leaves the problem, however, that the resulting organic film is rather permeable to water and oxygen and, hence, less resistant to rust.

[0025] In the organic film-coated plated steel sheet of the invention, rust resistance depends mainly upon the sacrificial action of rustproofness of Zn-base plating, so that the elution rate of Zn-based metal affects to a great extent the service life of the finished steel sheet. If it is possible to maintain stable Zn corrosive materials which are liable to be formed on the surface of a Zn-based plated layer placed on a substrate, then Zn shows a sharp decline in its elution rate. Thus, the organic film should most importantly have a role to retain the Zn corrosive materials and protect the Zn against elution. It is important that rust resistance can be attained in accordance with this invention only when the organic film is brought into cooperative relation with the Zn-based plated layer.

[0026] To hold stable the corrosive materials that corrode Zn, the exceptionally thin-walled organic film has been found to excel when it is very uniform in thickness.

[0027] FIG. 1 is a schematic representation as to the shape of an exceptionally thin-walled organic film formed on a base steel sheet by means of a conventional coater. In FIG. 2, there is schematically shown the extremely uniform thinness of an exceptionally thin-walled organic film formed on a base steel sheet by means of cathodic polymerization.

[0028] Thinner coatings are by nature difficult to control with a coater. The coating fails to follow regularly the concavities and convexities on the surface of a plated steel sheet 1, but tends to be deposited mainly in the concavities of a base steel sheet and thus forms an organic film 2 of irregular thickness as seen in FIG. 1. Especially when viewed microscopically the organic film 2 is quite irregular in its thickness. The coat thickness of this organic film is greater in the concavities of the substrate. This makes it adversely affect any subsequent electrodeposition painting. Conversely, the coat is extremely thin in the convexities of the substrate and, hence, incapable of maintaining stable the materials that tend to corrode the Zn, with the result that the Zn dissolves progressively and develops corrosion-originating pockets or points.

[0029] Cathodic polymerization contributes greatly to simplified control of coating thicknesses with adjustments in electrolytic time and electrical quantity. As shown in FIG. 2, the coating accurately and uniformly follows the concavities and convexities on the surface of a plated steel sheet 1, providing an organic film 3 that has good properties of electrodeposition ability, weldability or corrosion resistance.

[0030] We have found that when it is formed by cathodic polymerization upon the Zn-based metal, the organic film is capable of affording unique physical characteristics, i.e., coating thickness uniformity and retentivity of Zn corrosive materials, which have superior insulation and impermeability to water and oxygen than conventional organic films.

[0031] Of prime importance, in the practice of the present invention, is that a zinc- or zinc alloy-plated layer and the like should underlie the organic film. The beneficial effects of the organic film formed by cathodic polymerization are achievable only by bonding to such a plated layer.

[0032] It has also been found that in the practice of this invention conspicuous cost reductions can be brought about by shortened electrolysis and omitted baking operation.

[0033] The present invention will now be described in greater detail.

[0034] Intensive research has been conducted by us on the rustproofing mechanism of organic film-coated multi-

layered steel sheets commonly used for automobiles and on production methods enabling reductions in production equipment and reduced cost. Methods of film formation from cathodic polymerization have also been studied together with the properties of the resultant films. As a result, our new process has been discovered which does not require added plant investment and added production cost.

**[0035]** The organic film-coated plated steel sheet of the present invention has a zinc-based plated layer deposited inwardly of the surface of a steel sheet. By the term "the surface of a steel sheet" is meant either one or both of the surfaces of a base steel sheet. The term "zinc-based plating" means all types of plating using zinc that include but are not limited to platings with zinc alone, zinc alloys and zinc composite dispersions. Typical platings include zinc alone, platings with binary alloys such as Zn-Ni, Zn-Fe, Zn-Cr and the like, and platings with ternary alloys such as Zn-Ni-Cr, Zn-Co-Cr and the like. Platings with zinc composite dispersions may be used in which Zn-SiO<sub>2</sub>, Zn-Co-Cr-Al<sub>2</sub>O<sub>3</sub> and the like are included. The deposit amount of the plating is preferably in the range of not less than 10 g/m<sup>2</sup> and of not more than 90 g/m<sup>2</sup> from the point of view of corrosion resistance and cost control.

**[0036]** The organic film-coated plated steel sheet of the present invention has an organic film coated on a layer plated with a "zinc-based plating" as specified above. Coating of the organic film is achieved by cathodic reduction polymerization.

**[0037]** In the case of the cathodic polymerization coating according to the present invention, a given monomer bonds directly to the surface of the zinc-based plated layer by means of electrolysis and at the interface polymerizes into a film thereon. The resultant polymer also has firm bondability and, hence, adhesion to the plated layer surface and protects zinc corrosive materials from becoming eluted, thus leading to excellent and long-lasting corrosion resistance.

**[0038]** In addition, the film can be uniformly formed as discussed above, with a good and uniform fit to the shape of the plated layer. This prevents zinc from becoming locally eluted and thus reduces corrosion-originating points, thereby eventually improving corrosion resistance.

**[0039]** Conventional practice forms an organic film on a zinc-based plated steel sheet by painting, and in that instance, a chromium containing layer is often arranged as an intermediate layer. The reason behind this arrangement is that the organic film is not sufficiently adhesive to the plated metal surface when a coating is transferred with a coater on to the plated metal surface and then bonded by baking. By contrast, cathodic polymerization coating causes monomers to bond directly to the metal surface, and then to polymerize in place, causing the finished polymer to be bonded especially firmly to the metal surface. Accordingly, chromium containing compound treatment is not always necessary in accordance with this invention.

**[0040]** In the cathodic polymerization coating, the amount of organic film to be applied is preferably in the range of not less than 0.01 g/m<sup>2</sup> and of not more than 3 g/m<sup>2</sup>. Below 0.01 g/m<sup>2</sup> the amount is not effective to provide sufficient corrosion resistance. Above 3 g/m<sup>2</sup> the amount is too great and is less conducive to improved corrosion resistance and, moreover, is rather costly. Too thick a coating also invites difficulty in subsequent spot welding or electrodeposition painting.

**[0041]** As an organic film to be formed by polymerization, it is used cathodic polymerization.

**[0042]** Where cathodic polymerization is employed, an organic film may be formed preferably of one or more monomers chosen from among vinyl pyridine, acrylic acid, methacrylic acid, acrylic acid ester, methacrylic acid ester, acrylonitrile, styrene, crotonic acid and acetonitrile, and derivatives thereof.

**[0043]** Cathodic polymerization is advantageous in that the substrate metal is not dissolved, electricity is efficiently useful in forming an organic film, film formation is possible for shortened electrolysis, and no equipment is necessary for removal of dissolved metal from an electrolytically polymerized liquid.

**[0044]** In any case, cathodic polymerization according to the present invention should be effected preferably at a current density of not lower than 1 A/dm<sup>2</sup> for an electrolytic time of not longer than 10 seconds. In general, electrolytic polymerization has heretofore been conducted at a current density of lower than 1 A/dm<sup>2</sup>. Our experiments reveal, however, that current densities of below 1 A/dm<sup>2</sup> are responsible for film formation of thickness irregularity, namely coating unevenness, on the surface of a steel sheet as well as unsightly appearance of the sheet surface. This is assumed to be due to presence of an oxide of Zn.

**[0045]** When film formation is performed by electrolytic treatment and, as a typical example, when a metal plating such as Zn plating or the like is formed on a steel sheet, the substrate is usually pretreated as by electrolytic degreasing and pickling to remove oxides therefrom. These oxides lead not only to reduced electrolysis efficiency during plating, and to irregular film formation, but also to poor appearance. A substrate for use in the present invention is a steel sheet treated with a Zn-based plating, and, therefore, removal of oxides prior to cathodic polymerization is extremely adverse as it entails a damaged plated layer and added process steps. If it is conducted at a current density of lower than 1 A/dm<sup>2</sup>, cathodic polymerization is thought to cause an irregular film to be formed on the substrate surface.

**[0046]** To add to the above drawbacks, current densities of lower than 1 A/dm<sup>2</sup> need prolonged electrolysis to gain a desired coating thickness, which results in uneconomical production. Hence, a current density of not lower than 1 A/dm<sup>2</sup> and an electrolytic time of not longer than 10 seconds are preferred.

**[0047]** To further improve rust resistance, a chromium containing layer may be interposed between a first or innermost

layer treated with zinc or a zinc alloy and the like and an electrolytically polymerized film layer. Being quite costly, use of the chromium containing layer should be determined depending upon the extent of corrosion resistance desired.

[0048] In the present invention, the term "chromium containing layer" means not only a narrow sense of "chromate layer" comprising chromium oxide and chromium hydroxide, but also a "chromium plating layer" including metal chromium.

[0049] The coating amount of the chromium containing layer is preferably in the range of not less than 10 mg/m<sup>2</sup> and of not more than 500 mg/m<sup>2</sup>, expressed as Cr. Below 10 mg/m<sup>2</sup> is not effective to attain sufficient corrosion resistance from the chromium containing layer. Above 500 mg/m<sup>2</sup> produces no better results in improving such property and consumes excessive chromate and adds cost.

[0050] No particular restriction is imposed upon the method of chromium containing compound treatment to be used, and reactive chromium containing compound treatment, electrolytic chromium containing compound treatment, vapor deposition and the like may be employed. Film formation by means of electrolysis is thought to be most effective in view of the factor of cost reduction underlying the present invention.

#### Examples

[0051] With reference to the following examples, the present invention is further illustrated to demonstrate the beneficial effects thereof.

[0052] A 0.75 mm-thick, low-carbon steel sheet was pickled and degreased, followed by plating with Zn-based metal (where desired, further with chromate treatment). Film formation was then performed by means of cathodic polymerization to produce an organic film-coated steel sheet according to the invention. Performance evaluations were made on the resulting steel sheet for corrosion resistance, adhesion, spot weldability or electrodeposition ability.

[0053] To facilitate comparison, a 0.75 mm-thick, low-carbon steel sheet was pickled and degreased, followed by plating with a Zn-Ni alloy (Ni content: 12% by weight) (further with chromate treatment, if necessary). Epoxy resin was then painted with a painting coater to prepare an organic film-coated multi-layered steel sheet in common use. Another steel sheet was prepared in which cathodic polymerization treatment was performed on a base steel sheet with Zn-based plating omitted. The steel sheet was tested as in the inventive one.

#### Zn-based Plating

##### [0054]

Zn plating: Zn content - 100% by weight

Zn-Ni plating: Ni content - 12% by weight

Zn-Fe plating: Fe content - 10% by weight

Zn-Cr plating: Cr content - 10% by weight

Zn-Cr-Co-Al<sub>2</sub>O<sub>3</sub> plating: Cr content- 7% by weight, Co content - 0.7% by weight, Al<sub>2</sub>O<sub>3</sub> content - 1% by weight (as Al)

#### Chromium containing Compound Treatment

##### [0055]

reactive type: The steel sheet was immersed at 60°C for 3 seconds in a reactive chromium containing compound treatment liquid containing Cr and Fe ions and then washed with water.

electrolytic type: The steel sheet was cathodically electrolyzed at a current density of 80 A/dm<sup>2</sup> in a solution containing SO<sub>4</sub> ion at an H<sub>2</sub>SO<sub>4</sub>/CrO<sub>3</sub> = 1% ratio and then washed with water.

paintable type: The steel sheet was painted by a coater with a solution containing Cr ion at a Cr(III)/Cr(VI) = 1 ratio and then baked at an ultimate temperature of 150°C for 20 seconds.

#### Electrolytic Polymerization

[0056] Cathodic treatment was conducted at 40 to 60°C using a liquid containing 0.1 to 1 mol/l of a monomer. Purified water was used in principle as a solvent, but a mixture of methanol and water was employed when the monomer was less dissolvable. The methanol content was held to a minimum -- enough to dissolve the monomer. The resultant specimen was checked for its performance characteristics under a set of conditions indicated below.

Deposit Amount of Zinc-based Metal

[0057] Fluorescent X-radiation was performed by usual, well known means.

5 Coating Amount of Chromium

[0058] The quantity of Cr was measured from Cr counts by fluorescent X-radiation.

10 Coating Amount of Organic Film

[0059] The number of C counts was measured by fluorescent X-radiation.

Composite Cycle Corrosion Test

15 [0060] Corrosion testing was made as one cycle of (1) to (3), namely (1) spraying of a 5% NaCl solution for 4 hours in a thermostatic chamber of 35°C, (2) drying at 60°C for 2 hours, and (3) standing at 50°C and at 45 RH (wet) for 2 hours. Inspection was performed as to whether red rust developed. This testing was adjudged by the cycle required for red rust to form.

20 Paint Adhesion

[0061] Electrodeposition painting was effected on to the specimen (thickness: 20μm), which was then subjected to DuPont impact testing under the following conditions. Subsequently, adhesive tape testing was performed, and adhesion was determined by the peeling of an organic film.

25

DuPont impact testing: A sinker of 1 kg was allowed to drop at a distance of 50 cm from above on to the backside of the specimen by use of an impactor of 1/4 inch in diameter.

o: not peeled

x: peeled

30

Spot Weldability

35 [0062] To evaluate spot weldability, continuous welding was conducted at a pressure loading of 200 kgf and at a weld current of 9 kA, 10 Hz. In such instance, a welding chip was used which had been formed of an Al<sub>2</sub>O<sub>3</sub> dispersion type copper alloy and having a tip of 6 mm in diameter. Measurement was made of the points of counts continuously welded by the time that the nugget diameter had become below the standard diameter. Evaluation was based on the following reference standards.

- 40  
 ◎: above 3,000 points  
 ○: 2,001 - 3,000 points  
 △: 1,000 - 2,000 points  
 ×: below 1,000 points

Electrodeposition Ability

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[0063] Cathodic electrolytic treatment was conducted, with use of an automotive paint, in a bath of 28°C at 280 V for 3 minutes. The number of craters and gas pin-holes was inspected, and evaluation was based on the following reference standards.

- 50  
 ◎: number of craters and gas pin-holes - 0  
 ○: number of craters and gas pin-holes - 1 to 5  
 △: number of craters and gas pin-holes - 6 to 10  
 ×: number of craters and gas pin-holes - above 11

55 Cost Evaluation of Equipment

[0064] Production should be made feasible with effective use of post-treatment facilities such as reserve tanks of ordinary Zn-base plating equipment. The details of evaluation were based on the following criteria.

- ⑤ When electrolysis is effected at the same line speed as in Zn-based plating, production can be considered feasible with 3 or less plating tanks (expected to be substantially without added plant installation).
- : When electrolysis is effected at the same line speed as in Zn-based plating, production can be considered feasible with 5 or less plating tanks (expected to be substantially without added plant installation, or with a small scale of additional installations, if any).
- ×: New plants can be considered necessary to be installed.

#### Cost Evaluation of Productivity

[0065]

- ⑤ Production can be considered feasible as integrated with ordinary Zn-based plating equipment, and with least control factors.
- : Production can be considered feasible as integrated with ordinary Zn-based plating equipment, but with additional control factors.
- ×: Coiling can be considered to be firstly needed after common plating with Zn-based metal, followed by transfer and treatment of the coil at separate equipment.

[0066] The test results are listed in Tables 1 (1) to 1 (3).

[0067] Inventive Examples 1 to 53 are all satisfactory in respect of all of the characteristics tested. These examples have demonstrated those steel sheets for automotive use that excel in corrosion resistance, weldability, electrodeposition paintability or paint adhesion with reduced equipment requirements and reduced cost.

[0068] Comparative Examples 1 and 2 were insufficient with respect to corrosion resistance as they were devoid of a Zn-based plated layer that is an important component for the practice of the present invention.

[0069] In Comparative Examples 3 and 4, an electrolytically polymerized film was formed in a larger coating amount. To this end, a large number of plating tanks and a large floor space therefor have been found to be necessary. Zn-based plating equipment in common use for rust-proof automotive steel sheets can no longer meet automobile manufacturers' requirements with consequential need for new plant investments. In addition to these problems, the steel sheets of Comparative Examples 3 and 4 are not sufficient in improving corrosion resistance as they are free from a Zn-based plated layer as contrasted to the inventive steel sheets and, conversely, are deteriorative in respect of weldability and electrodeposition paint ability.

[0070] Comparative Examples 5 to 7 revealed reduced adhesion to a Zn-based plated layer and poor corrosion resistance due to omission of an electrolytically polymerized film and of chromium containing compound treatment.

[0071] Comparative Example 8 is an organic film-coated multi-layered steel sheet recently used as a rustproof steel sheet for automobiles, but is highly susceptible to a rise in cost from the point of view of equipment and production.



Table 1 - 1

## Example

No.	Zn-based of Plating		Chromate		Cathodic Polymerization			Cost Evaluation		Performance Test			
	Kind	Amount (g/m <sup>2</sup> )	Type	Amount (mg/m <sup>2</sup> )	Monomer	Condition	Coating Amount (g/m <sup>2</sup> )	Equipment	Productivity	CCT (cycle)	Adhesion	Weldability	Electrodeposition ability
1	Zn-Ni plating	20	-	-	Vinyl Pyridine	-10A/dm <sup>2</sup> × 5sec	1.0	•	•	120	o	•	•
2	Zn-Ni plating	20	-	-	Acrylonitrile	-5A/dm <sup>2</sup> × 7sec	0.01	•	•	100	o	•	•
3	Zn-Ni plating	20	-	-	Styrene	-30A/dm <sup>2</sup> × 5sec	0.1	•	•	100	o	•	•
4	Zn-Ni plating	20	-	-	Acrylic Acid	-20A/dm <sup>2</sup> × 3sec	0.5	•	•	110	o	•	•
5	Zn-Ni plating	20	-	-	Acetonitrile	-1A/dm <sup>2</sup> × 10sec	1.2	•	•	120	o	•	•
6	Zn-Ni plating	20	-	-	Crotonic Acid	-20A/dm <sup>2</sup> × 5sec	0.3	•	•	110	o	•	•
7	Zn-Ni plating	20	-	-	Methyl Methacrylate	-5A/dm <sup>2</sup> × 10sec	2.0	•	•	130	o	•	•
8	Zn-Ni plating	10	-	-	Vinyl Pyridine	-10A/dm <sup>2</sup> × 5sec	1.0	•	•	100	o	•	•
9	Zn-Ni plating	30	-	-	Acrylonitrile	-5A/dm <sup>2</sup> × 7sec	0.01	•	•	150	o	•	•
10	Zn-Ni plating	60	-	-	Styrene	-30A/dm <sup>2</sup> × 5sec	0.1	•	•	250	o	•	•

Table 1 - 2

Example

No.	Zn-based of Plating		Chromate		Cathodic Polymerization			Cost Evaluation		Performance Test			
	Kind	Amount (g/m <sup>2</sup> )	Type	Amount (mg/m <sup>2</sup> )	Monomer	Condition	Coating Amount (g/m <sup>2</sup> )	Equipment	Productivity	CCT (cycle)	Adhesion	Weldability	Electrodeposition ability
11	Zn-Ni plating	5	-	-	Acrylic Acid	-20A/dm <sup>2</sup> × 3sec	0.5	•	•	20	o	•	•
12	Zn-Ni plating	80	-	-	Acrylonitrile	-1A/dm <sup>2</sup> × 10sec	1.2	•	o	150	o	•	•
13	Zn-Ni plating	20	Reactive	50	Vinyl Pyridine	-10A/dm <sup>2</sup> × 5sec	0.02	o	o	120	o	o	o
14	Zn-Ni plating	20	Electrolytic	50	Vinyl Pyridine	-10A/dm <sup>2</sup> × 5sec	0.8	o	o	150	o	o	o
15	Zn-Ni plating	20	Electrolytic	5	Vinyl Pyridine	-10A/dm <sup>2</sup> × 5sec	0.8	o	o	120	o	•	•
16	Zn-Ni plating	20	Electrolytic	10	Vinyl Pyridine	-10A/dm <sup>2</sup> × 5sec	0.8	o	o	130	o	o	o
17	Zn-Ni plating	20	Electrolytic	100	Vinyl Pyridine	-10A/dm <sup>2</sup> × 5sec	0.8	o	o	170	o	o	o
18	Zn-Ni plating	20	Electrolytic	300	Acrylic Acid	-20A/dm <sup>2</sup> × 3sec	0.4	o	o	170	o	o	o
19	Zn-Ni plating	20	Electrolytic	300	Vinyl Pyridine	-10A/dm <sup>2</sup> × 5sec	0.8	o	o	200	o	o	o
20	Zn-Ni plating	20	Electrolytic	500	Vinyl Pyridine	-10A/dm <sup>2</sup> × 5sec	0.8	o	o	300	o	o	o

Table 1 - 3

Example

No.	Zn-based of Plating		Chromate		Cathodic Polymerization			Cost Evaluation		Performance Test			
	Kind	Amount (g/m <sup>2</sup> )	Type	Amount (mg/m <sup>2</sup> )	Monomer	Condition	Coating Amount (g/m <sup>2</sup> )	Equipment	Productivity	CCT (cycle)	Adhesion	Weldability	Electrodeposition ability
21	Zn-Ni plating	20	Electrolytic	700	Vinyl Pyridine	-10A/dm <sup>2</sup> x 5sec	0.8	○	○	400	○	+	+
22	Zn-plating	20	-	-	Vinyl Pyridine	-10A/dm <sup>2</sup> x 5sec	1.0	●	●	80	○	●	●
23	Zn-plating	20	-	-	Acrylonitrile	-5A/dm <sup>2</sup> x 7sec	0.01	●	●	60	○	●	●
24	Zn-plating	20	-	-	Styrene	-30A/dm <sup>2</sup> x 5sec	0.1	●	●	70	○	●	●
25	Zn-plating	20	-	-	Acrylic Acid	-20A/dm <sup>2</sup> x 3sec	0.5	●	●	80	○	●	●
26	Zn-plating	20	Electrolytic	50	Vinyl Pyridine	-10A/dm <sup>2</sup> x 5sec	0.8	○	○	100	○	○	○
27	Zn-plating	20	Electrolytic	50	Acrylonitrile	-5A/dm <sup>2</sup> x 7sec	0.005	○	○	60	○	○	○
28	Zn-plating	20	Electrolytic	50	Styrene	-30A/dm <sup>2</sup> x 5sec	0.1	○	○	90	○	○	○
29	Zn-plating	20	Electrolytic	50	Acrylic Acid	-20A/dm <sup>2</sup> x 3sec	0.5	○	○	100	○	○	○
30	Zn-Cr plating	20	-	-	Vinyl Pyridine	-15A/dm <sup>2</sup> x 5sec	0.8	●	●	200	○	●	●

Table 1 - 4

## Example

No.	Zn-based of Plating		Chromate		Cathodic Polymerization			Cost Evaluation		Performance Test			
	Kind	Amount (g/m <sup>2</sup> )	Type	Amount (mg/m <sup>2</sup> )	Monomer	Condition	Coating Amount (g/m <sup>2</sup> )	Equipment	Productivity	CCT (cycle)	Adhesion	Held-ability	Electrodeposition ability
31	Zn-Cr plating	20	-	-	Acrylonitrile	-10A/dm <sup>2</sup> x 7sec	0.005	•	•	150	o	•	•
32	Zn-Cr plating	20	-	-	Styrene	-30A/dm <sup>2</sup> x 5sec	0.05	•	•	180	o	•	•
33	Zn-Cr plating	20	-	-	Acrylic Acid	-20A/dm <sup>2</sup> x 5sec	0.4	•	•	200	o	•	•
34	Zn-Cr plating	20	Electrolytic	50	Vinyl Pyridine	-10A/dm <sup>2</sup> x 5sec	0.8	o	o	260	o	o	o
35	Zn-Cr plating	20	Electrolytic	50	Acrylonitrile	-5A/dm <sup>2</sup> x 7sec	0.005	o	o	200	o	o	o
36	Zn-Cr plating	20	Electrolytic	50	Styrene	-30A/dm <sup>2</sup> x 5sec	0.05	o	o	230	o	o	o
37	Zn-Cr plating	20	Electrolytic	50	Acrylic Acid	-20A/dm <sup>2</sup> x 5sec	0.4	o	o	160	o	o	o
38	Zn-Fe plating	20	-	-	Vinyl Pyridine	-10A/dm <sup>2</sup> x 5sec	1.0	•	•	100	o	•	•
39	Zn-Fe plating	20	-	-	Acrylonitrile	-5A/dm <sup>2</sup> x 7sec	0.01	•	•	80	o	•	•
40	Zn-Fe plating	20	-	-	Styrene	-30A/dm <sup>2</sup> x 5sec	0.1	•	•	90	o	•	•

Table 1 - 5

Example

Example

No.	Zn-based of Plating		Chromate		Cathodic Polymerization			Cost Evaluation		Performance Test			
	Kind	Amount (g/m <sup>2</sup> )	Type	Amount mg/m <sup>2</sup> )	Monomer	Condition	Coating Amount (g/m <sup>2</sup> )	Equip-ment	Product-ivity	CCT (cycle)	Adhe-sion	Weld-abil-ity	Electro deposi-tion ability
41	Zn-Fe plating	20	-	-	Acrylic Acid	-20A/dm <sup>2</sup> x 3sec	0.5	•	•	100	o	•	•
42	Zn-Fe plating	20	*Elect	50	Vinyl Pyridine	-10A/dm <sup>2</sup> x 5sec	0.8	o	o	130	o	o	o
43	Zn-Fe plating	20	*Elect	50	Acrylonitrile	-5A/dm <sup>2</sup> x 7sec	0.005	o	o	80	o	o	o
44	Zn-Fe plating	20	*Elect	50	Styrene	-30A/dm <sup>2</sup> x 5sec	0.1	o	o	110	o	o	o
45	Zn-Fe plating	20	*Elect	50	Acrylic Acid	-20A/dm <sup>2</sup> x 3sec	0.5	o	o	120	o	o	o
46	Zn-Cr-Co-Al <sub>2</sub> O <sub>3</sub> plating	20	-	-	Vinyl Pyridine	-15A/dm <sup>2</sup> x 5sec	0.8	•	•	230	o	•	•
47	Zn-Cr-Co-Al <sub>2</sub> O <sub>3</sub> plating	20	-	-	Acrylonitrile	-10A/dm <sup>2</sup> x 7sec	0.005	•	•	180	o	•	•
48	Zn-Cr-Co-Al <sub>2</sub> O <sub>3</sub> plating	20	-	-	Styrene	-30A/dm <sup>2</sup> x 5sec	0.05	•	•	210	o	•	•
49	Zn-Cr-Co-Al <sub>2</sub> O <sub>3</sub> plating	20	-	-	Acrylic Acid	-20A/dm <sup>2</sup> x 5sec	0.4	•	•	230	o	•	•
50	Zn-Cr-Co-Al <sub>2</sub> O <sub>3</sub> plating	20	*Elect	50	Vinyl Pyridine	-10A/dm <sup>2</sup> x 5sec	0.8	o	o	300	o	o	o

\*Elect means Electrolytic.

Table 1 - 6

Example

No.	Zn-based of Plating		Chromate		Cathodic Polymerization			Cost Evaluation		Performance Test			
	Kind	Amount (g/dm <sup>2</sup> )	Type	Amount (mg/dm <sup>2</sup> )	Monomer	Condition	Coating Amount (g/dm <sup>2</sup> )	Equip- ment	Produc- tivity	CCT (cycle)	Adhe- sion ity	Weld- abil- ity	Electro- deposi- tion ability
51	Zn-Cr-Co-Al <sub>2</sub> O <sub>3</sub> plating	20	*Elect	50	Acrylonitrile	-5A/dm <sup>2</sup> × 7sec	0.005	o	o	230	o	o	o
52	Zn-Cr-Co-Al <sub>2</sub> O <sub>3</sub> plating	20	*Elect	50	Styrene	-30A/dm <sup>2</sup> × 5sec	0.05	o	o	260	o	o	o
53	Zn-Cr-Co-Al <sub>2</sub> O <sub>3</sub> plating	20	*Elect	50	Acrylic Acid	-20A/dm <sup>2</sup> × 3sec	0.4	o	o	200	o	o	o

\*Elect means Electrolytic.

Table 1 - 8

## Comparative Example

Comparative Example													
No.	Zn-based of Plating		Chronate		Cathodic Polymerization			Cost Evaluation		Performance Test			
	Kind	Amount (g/m <sup>2</sup> )	Type	Amount (mg/m <sup>2</sup> )	Monomer	Condition	Coating Amount (g/m <sup>2</sup> )	Equip-ment	Productivity	CCT (cycle)	Adhe-sion	Weld-ability	Electro-deposi-tion ability
1	-	-	-	-	Vinyl Pyridine	-10A/dm <sup>2</sup> × 5sec	1.0	●	●	3	○	●	●
2	-	-	-	-	Acrylonitrile	-5A/dm <sup>2</sup> × 7sec	0.005	●	●	1	○	●	●
3	-	-	-	-	Vinyl Pyridine	-10A/dm <sup>2</sup> × 3min	15	×	○	7	○	×	×
4	-	-	-	-	Acrylonitrile	-5A/dm <sup>2</sup> × 5min	10	×	○	10	○	×	×
5	Zn plating	20	-	-	-	-	-	●	●	40	●	●	●
6	Zn-Ni plating	20	-	-	-	-	-	●	●	60	×	●	●
7	Zn-Ni plating	20	-	-	-	Coater-painted *	0.5	×	×	60	×	●	●
8	Zn-Ni plating	20	paintable	50	-	Coater-painted *	0.5	×	×	90	○	○	○

\* Epoxy resin was painted by coater.

[0072] According to the present invention, an organic film-coated plated steel sheet is provided which is resistant to corrosion, weldable, paintable by electrodeposition or adhesive to paints, and is excellent as a rust-proof steel sheet particularly for use in automobile bodies.

[0073] Also provided is a process for producing such steel with saved equipment and with reduced production cost which could not be afforded by the prior art.

# Claims

1. A process for the production of an organic film-coated plated steel sheet, which comprises the steps of:  
plating a zinc-based metal on either one or both surfaces of a steel sheet to form a zinc-based plated steel sheet; and  
subsequently carrying out a cathodic polymerization of at least one organic monomer in an electrolytic liquid to form an organic film on said zinc-based plated steel sheet.
2. The process according to claim 1, further comprising the steps of:  
treating at least one surface of said zinc-based plated steel sheet with a chromium-containing compound solution to form a chromium-coated steel sheet;  
subsequently carrying out said cathodic polymerization of a monomer on said chromium-treated steel sheet;  
and  
adhering an organic film layer to said chromium-coated steel sheet.
3. The process according to claim 1, wherein said plating of zinc-based metal is deposited in an amount of 10 to 90 g/m<sup>2</sup>, and said organic film is adhered in an amount of 0.01 to 3 g/m<sup>2</sup>.
4. The process according to claim 2, wherein said plating of zinc-based metal is deposited in an amount of 10 to 90 g/m<sup>2</sup>, said chromium-containing compound treatment is conducted in a coating amount of 10 to 500 mg/m<sup>2</sup> in terms of Cr, and said organic film is adhered in an amount of 0.01 to 3 g/m<sup>2</sup>.
5. The process according to claim 1, wherein said at least one monomer is selected from the group consisting of vinyl pyridine, acrylic acid, methacrylic acid, acrylic acid ester, methacrylic acid ester, acrylonitrile, styrene, crotonic acid, acetonitrile and derivatives thereof.
6. The process according to claim 3, wherein said cathodic polymerization is effected in a current density of not lower than 1 A/dm<sup>2</sup> and for an electrolytic time of not longer than 10 seconds.

# Patentansprüche

1. Verfahren zur Herstellung eines mit einem organischen Film beschichteten, galvanisierten Stahlbleches in folgenden Stufen:  
galvanisches Abscheiden eines Metalls auf Zinkbasis auf entweder eine oder beide Oberfläche(n) eines Stahlblechs zur Herstellung eines galvanisch verzinkten Stahlblechs und  
anschließendes kathodisches Polymerisieren mindestens eines organischen Monomers in einem flüssigen Elektrolyten zur Bildung eines organischen Films auf dem galvanisch verzinkten Stahlblech.
2. Verfahren nach Anspruch 1, bei welchem zusätzlich die folgenden Stufen durchgeführt werden:  
Behandeln mindestens einer Oberfläche des galvanisch verzinkten Stahlblechs mit einer Lösung einer chromhaltigen Verbindung zur Herstellung eines mit Chrom beschichteten Stahlblechs;  
anschließendes kathodisches Polymerisieren eines Monomers auf dem chrombehandelten Stahlblech und  
Befestigen eines schichtförmigen organischen Films auf dem chrombehandelten Stahlblech.



3. Verfahren nach Anspruch 1, wobei das galvanisch abgeschiedene Metall auf Zinkbasis in einer Menge von 10 bis 90 g/m<sup>2</sup> abgelagert und der organische Film in einer Menge von 0,01 bis 3 g/m<sup>2</sup> befestigt bzw. zum Haften gebracht werden.
- 5 4. Verfahren nach Anspruch 2, wobei das galvanisch abgeschiedene Metall auf Zinkbasis in einer Menge von 10 bis 90 g/m<sup>2</sup> abgelagert ist, die Behandlung mit der chromhaltigen Verbindung in einer Auftragsmenge von 10 bis 500 mg/m<sup>2</sup>, ausgedrückt als Cr, erfolgt und der organische Film in einer Menge von 0,01 bis 3 g/m<sup>2</sup> befestigt bzw. zum Haften gebracht werden.
- 10 5. Verfahren nach Anspruch 1, wobei das mindestens eine Monomer aus der Gruppe, bestehend aus Vinylpyridin, Acrylsäure, Methacrylsäure, Acrylsäureester, Methacrylsäureester, Acrylnitril, Styrol, Crotonsäure, Acetonitril oder Derivaten derselben, ausgewählt wird.
- 15 6. Verfahren nach Anspruch 3, wobei die kathodische Polymerisation bei einer Stromdichte von nicht weniger als 1 A/dm<sup>2</sup> und während einer Elektrolysedauer von nicht länger als 10 s durchgeführt wird.

#### Revendications

- 20 1. Procédé pour la production d'une tôle d'acier plaquée revêtue d'un film organique, qui comprend les étapes consistant :  
à plaquer un métal à base de zinc sur l'une des surfaces ou les deux d'une tôle d'acier pour former une tôle d'acier plaquée de métal à base de zinc ; et  
25 à effectuer ensuite une polymérisation cathodique d'au moins un monomère organique dans un liquide électrolytique pour former un film organique sur ladite tôle d'acier plaquée de métal à base de zinc.
2. Procédé selon la revendication 1, comprenant en outre les étapes consistant :  
30 à traiter au moins une surface de ladite tôle d'acier plaquée revêtue de métal à base de zinc avec une solution de composé contenant du chrome pour former une tôle d'acier revêtue de chrome ;  
puis à effectuer ladite polymérisation cathodique d'un monomère sur ladite tôle d'acier traitée par du chrome ; et  
à faire adhérer une couche de film organique sur ladite tôle d'acier revêtue de chrome.
- 35 3. Procédé selon la revendication 1, dans lequel ledit placage de métal à base de zinc est déposé en une quantité de 10 à 90 g/m<sup>2</sup>, et ledit film organique est adhérent en une quantité de 0,01 à 3 g/m<sup>2</sup>.
4. Procédé selon la revendication 2, dans lequel ledit placage de métal à base de zinc est déposé en une quantité de 10 à 90 g/m<sup>2</sup>, ledit traitement avec un composé contenant du chrome est effectué en une quantité de revêtement  
40 de 10 à 500 mg/m<sup>2</sup> en termes de Cr, et ledit film organique est adhérent en une quantité de 0,01 à 3 g/m<sup>2</sup>.
5. Procédé selon la revendication 1, dans lequel ledit au moins un monomère est choisi dans le groupe constitué par la vinylpyridine, l'acide acrylique, l'acide méthacrylique, un ester de l'acide acrylique, un ester de l'acide méthacrylique, l'acrylonitrile, le styrène, l'acide crotonique, l'acétonitrile et des dérivés de ceux-ci.  
45
6. Procédé selon la revendication 3, dans lequel ladite polymérisation cathodique est effectuée à une densité de courant non inférieure à 1 A/dm<sup>2</sup> et pendant un temps d'électrolyse non supérieur à 10 s.

50

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FIG. 1  
CONVENTIONAL

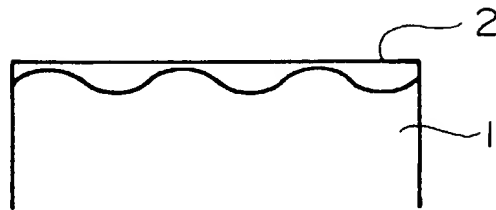


FIG. 2

